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Orientations of the Molecules in Naphthalene and Anthracene Crystals.

BY

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ABSTRACT.

It has been found that the intensities of X-ray diffraction from naphthalene and anthracene crystals do not conform to the orientations of the molecules along any cell face. By the "trial and error" method of analysis it has been found that the molecules are inclined to the cell faces, the correct positions being obtained by first placing them along the plane and then by two successive rotations about the '*b*' and the '*c*' axes. The rotations about the b-axis for the two molecules in the unit cell are equal but opposite, while about '*c*' they are in the same direction in conformity with the space-group C_{2h}^5. The amounts of rotations for naphthalene are 25° and 12° respectively and those for anthracene are 25° and 9°. All the benzene rings in the same molecule are in the same plane and the rings are practically regular hexagons. The structure obtained as the result of the present investigations is in conformity with the magnetic and the optical properties of these crystals.

1. *Introduction.*

The nature and dimensions of unit cells of naphthalene and anthracene were determined by Bragg by the reflection method. His results conformed to the space-group C_{2h}^5 for both the crystals with cell dimensions

$a=8{\cdot}34$ A°., $b=6{\cdot}05$ A°., $c=8{\cdot}68$ A°. and $\beta=122°44'$, for naphthalene,[1] and

$a=8{\cdot}58$ A°., $b=6{\cdot}02$ A°., $c=11{\cdot}18$ A°., and $\beta=125°$ for anthracene.[2]

It was also mentioned there that these crystals are better understood if the planes of the molecules lie nearer the *ac* plane than if they do so near the *bc* planes, since the *b*-axis is shorter than the *a*-axis. On the other hand it has been shown by S. Bhagavantam[3] that the results of his measurements on the diamagnetic susceptibilities and refractive indices for the different crystal axes definitely require that the planes of the molecules should be so oriented that the optical polarisability should be minimum and the diamagnetic susceptibility should be maximum normal to the *bc* plane. This can happen only if the plane of the molecule lies nearer the *bc* plane than the *ac* plane.

In view of the important position of naphthalene and anthracene among the aromatic series of compounds, it is useful to make an investigation into the position of the carbon atoms in these crystals by means of X-rays. These crystals have two molecules per unit cell and hence the unit cell contains 20 and 28 carbon atoms respectively. As the crystals have four elements of symmetry it is necessary to determine the positions of 5 and 7 atoms respectively. Thus the number of independent parameters that are to be determined are 15 and 21 respectively if we neglect the effects of the hydrogen atoms. The method of two-dimensional Fourier analysis is applicable for this purpose in the form presented by W. L. Bragg,[4] but it requires the determinations of absolute intensities for a large number of reflections while the

[1] Bragg, Proc. Phys. Soc., Vol. 34, p. 33, 1921-22.

[2] Bragg, Proc. Phys. Soc., Vol. 35, p. 167, 1922-23.

[3] Bhagavantam, Proc. Roy. Soc., Vol. 124, p. 545, 1929; Ind. Journ. Phys., Vol. 4, pt. 1, p. 1, 1929.

[4] W. L. Bragg, Proc. Roy. Soc., Vol. 123, p. 537, 1929.

choice of proper signs of the different terms of the series give it the character of the method of trial and error. The method of Ott,[1] on the other hand, requires determinations of relative intensities of a fewer number of reflections, but the large number of unknown parameters makes the equations complicated. The method that has been followed in this investigation is, accordingly, the method of trial and error.

2. *Experimental.*

For this investigation a Shearer X-ray tube run by an induction coil was used. Powder photographs were taken with copper radiations filtered through a solution of nickel nitrate. The powder was contained in a narrow tube of cigarette paper. The exposure was adjusted so that the strongest reflection did not suffer over-exposure and blackening of the photographic plate for strong reflections only were compared by means of a microphotometer. The integrated intensities for reflections from different planes are given in the second Columns of Tables I and II for naphthalene and anthracene. The third column gives the structure-factors. For their calculation, the crystals were regarded as ideally imperfect and the structure factors were obtained from the relations

$$\frac{F_2}{F_1} = \sqrt{\frac{p_1(1+\cos^2 2\theta_1)\sin\theta_2 \tan 2\theta_2}{p_2(1+\cos^2 2\theta_2)\sin\theta_1 \tan 2\theta_1}} \cdot \frac{P_2}{P_1}.$$

Where F_1, p_1, θ_1, P_1 are the structure factor, the number of planes of the type, the glancing angle, and the integrated intensities for reflection from a standard plane, namely, the 001 face, while F_2, p_2, θ_2, P_2 are the corresponding quantities for any other reflection. For the second and the third columns of the tables P_1 is taken as 100 and F as unity respectively.

For the oscillation photographs, the substances were

[1] Ott. Zeits. f. Kryst. Bd. 66, p. 136, 1928.

crystallised from alcohol, and crystalline plates were obtained. Photographs about the "a" and the "b" axes were taken. The integrated intensities for reflections from the 001 face and its higher orders were compared by means of a microphotometer. As the intensities of reflections from the other faces depended on some factors that could not be known accurately, these intensities were recorded by eye-estimation, and hence they are only qualitative. The results for the integrated intensities for naphthalene and anthracene crystals are given in Tables III and IV. The integrated intensity of the 001 reflection is taken as 100 and the other intensities are expressed in terms of that in the second column. The structure factor in the third column is given by the relation

$$\frac{\omega_2 P_2}{\omega_1 P_1} = \frac{F_2^2}{F_1^2} \cdot \frac{\dfrac{1+\cos^2 2\theta_2}{\sin 2\theta_2}}{\dfrac{1+\cos^2 2\theta_1}{\sin 2\theta_1}}$$

$$\text{or } \frac{F_2}{F_1} = \sqrt{\frac{\sin 2\theta_2(1+\cos^2 2\theta_1)}{\sin 2\theta_1(1+\cos^2 2\theta_2)} \cdot \frac{\omega_2 P_2}{\omega_1 P_1}}$$

where ω is the angular velocity of the crystal at the instant of reflection.

TABLE I.

Intense Rings in the Powder Photographs of Naphthalene.

Millerian Indices.	Integrated Intensity.	Molecular Structure Factor.
001	100	1
200	86	1·34
110	105	1·19
210	80	1·02
211	85	0·92
$20\bar{1}$	70	1·57
$11\bar{1}$	20	0·47

TABLE II.

Intense Rings in the Powder Photograph of Anthracene

Millerian Indices.	Integrated Intensity.	Molecular Structure Factor.
001	100	1
200	52	1·81
110	250	2·09
210	54	1·54
211	46	1·19
201	29	0·93

TABLE III.

Reflection from 001 Face and its Higher Orders, Naphthalene.

Indices.	Integrated Intensity.	Molecular Structure Factor,	Positional Structure Factor.
001	100	1	1
002	27	0·53	0·83
003	16	0·42	0·91
004		0·14	0·42

TABLE IV.

Reflections from 001 Face and its Higher Orders, Anthracene.

Indices.	Integrated Intensity.	Molecular Structure Factor.	Positional Structure Factor.
001	100	1	1
002	28	0·52	0·94
003	6·5	0·31	0·80
004	11	0·44	1·22
005	1·5	0·17	0·58

3. *The Nature of the Benzene Rings in Naphthalene.*

Raman and Bhagavantam [1] have concluded from the close resemblance of the optical and magnetic anisotropies of graphite and a large number of crystals of aromatic compounds that the valency bonds of the carbon atoms in aromatic compounds are identical with those of graphite. Ott [2] has shown that in graphite the carbon atoms form plane hexagonal rings so that each carbon atom has three of its valency bonds in the same plane. It is thus quite probable that the benzene rings in aromatic compounds are plane hexagonal rings. This has been verified by the works of K. Lonsdale [3] who has made a thorough investigation of the positions of the carbon atoms in hexamethylbenzene. The following results were obtained by her :—

(1) The benzene ring is hexagonal or pseudo-hexagonal.

(2) The diameter of a carbon atom in an aromatic compound is 1·42 in conformity with the results of Ott.

(3) The carbon atoms in the benzene ring are in one plane and the carbon atoms of the methyl groups lie in the same plane.

From these facts it may be safely concluded that also for the benzene rings in naphthalene the carbon atoms lie in a plane, and are arranged in a hexagonal ring which may possibly be either elongated or contracted along the length of the molecule and the diameter of a carbon atom is 1·42 A°. Further, since the crystal belongs to the space-group C^5_{2h} and a cell contains two molecules only, the molecules should possess a centre of symmetry. Two plane benzene rings attached together by a side, can have a centre of symmetry only if they are in the same plane.

Starting with these assumptions as working hypothesis

[1] Raman and Bhagavantam, Ind. Journ. Phys., Vol. 4, pt. 1, p. 57, 1929.
[2] Ott, Ann. d. Phys., Vol. 85, p. 81. 1928.
[3] K. Lonsdale, Proc. Roy. Soc., Vol. 123, p. 494, 1929.

we shall investigate into the orientations of the benzene rings and then shall examine the effects of deviations from these assumptions on the reflections from different planes.

Let us first try whether either of the ways of placing the molecule, that have been suggested by Bragg and Bhagavantam, represents facts. The former investigator suggested that the molecule is in the '*ac*' plane, while according to the latter it is in the '*bc*' plane. In Table V the structure factors for reflections from different planes are given as calculated according to these two ways of placing the molecules by the equation

$$F_m = F_a \times \sum_k \cos \frac{2\pi z_k}{d},$$

where F_m and F_a are the molecular and the atomic structure factor, z, the normal distance of an atom from the midplane and d the normal distance for two consecutive parallel planes. For the atomic structure factors, the values are taken as the same as those for graphite and are obtained from the structure factor curve for graphite given in Lonsdale's paper.

TABLE V.

Indices.	Structure Factor. Mol. in 010 plane.	Mol. in 100 plane.	Bragg's Remark on Intensity.
001	18·80	20·1	Very strong.
200	7·54	34·6	Strong.
020	31·20	11·2	Very strong.
110	27·47	20·8	Strong.
$11\bar{1}$	14·20	5·1	Moderate.
$20\bar{1}$	0·27	14·6	Strong.
$02\bar{1}$	10·20	6·8	Very weak.
$20\bar{1}$	5·70	9·6	Very weak.
210	0	0	Strong.
$21\bar{1}$	0	0	Strong.

The second and third columns of the table contain the calculated structure factors considering the molecules to be placed along the '*bc*' planes and along the '*ac*' planes respectively. The results show that though the latter column gives better agreement with the fourth column where Bragg's remarks on the intensities are given, the discrepancies for some of the planes are significant, particularly for the planes $11\bar{1}$, 210 and $21\bar{1}$. This definitely shows that the molecules can be neither in the '*ac*' planes nor in the '*bc*' planes. Trial was further made to get agreement by supposing the molecules to be puckered, but no amount of puckering would give rise to sufficiently large values of the structure factors for these planes. Thus it follows that the molecules must be inclined to the axial planes, and we are to determine these inclinations. Let us designate the two molecules in the unit cell by M_1 and M_2 the former being at the corner of the cell. Suppose the molecule M_1 is first placed along the '*bc*' plane with AB, Fig. 1, along the '*b*' axis and then is brought to the correct position by the following successive rotations:—

(1) through θ about the *c*-axis

(2) through ϕ about the *b*-axis

(3) through ψ about an axis normal to the '*ab*' plane, which we shall call the c^* axis.

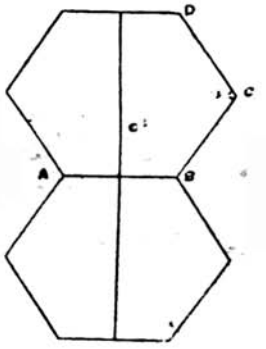

Fig. 1

In order that M_2 may be a glide plane reflection of M_1 it should have rotations of $-\theta$, ϕ and $-\psi$ about the corres-

ponding axes. Let us assume the angle BCD (Fig. 1) is $120° + \chi$, then the parameters that fix the positions of the carbon atoms and which we are to determine are θ, ϕ, ψ and χ.

Fig. 2

4. *Determination of the Parameters.*

The z co-ordinate of any atom in M_1 will be the same as that for a corresponding atom M_2, as M_2 is obtained from M_1 by a glide plane reflection, the gliding taking place parallel to 'a' and the plane of reflection being normal to the z-axis. Corresponding to each atom in the same molecule there will be another having the same numerical value of z but of opposite sign, since the molecule possesses a centre of symmetry. Thus the twenty carbon atoms will have pairs of the following 10 values of the z co-ordinates

$$z_1,\ z_2,\ z_3,\ z_4,\ z_5$$

$$-z_1,\ -z_2,\ -z_3,\ -z_4,\ -z_5$$

Let their ratios to the c-axis be respectively

$$\pm\rho_1,\ \pm\rho_2,\ \pm\rho_3,\ \pm\rho_4 \text{ and } \pm\rho_5$$

The ρ's are connected to the dimensions of the benzene rings by the following relations.

$$\rho_2=\rho_p+\rho_q$$

$$\rho_3=2\rho_p+\rho_1$$

$$\rho_4=2\rho_p-\rho_1$$

$$\rho_5=\rho_p-\rho_q$$

where the ratios to c of the z co-ordinates of P is ρ_p and of C is $\rho_p \times \rho_q$. Since OA, the diameter of a carbon atom is 0·71A° cannot be greater than $\frac{1}{12}$ and since the length of the molecule cannot be very far from the c-axis, the value of ρ_p will be considerably less than $\frac{1}{12}$ and hence it is sufficient to search for it only up to this value.

The values for the integrated intensities for the different reflections from the 001 plane and the corresponding molecular structure factors are given in Table III. In the fourth column are given the positional structure factors obtained by dividing the molecular structure factors by the atomic which is obtained from the curve for graphite given in Lonsdale's paper. For the last three columns the structure factor for the first order reflection is taken as unity. The positional structure factor for these reflections is given by the relation

$$S_n=\sum_k e^{-2\pi i n P_k}$$

where n is the order of reflection ; the summations are to be carried over all the atoms, so that we have,

$$\begin{aligned} S_n &= \sum_k \cos 2\pi n\rho_k \\ &= 4\sum_k \cos n a_k \\ &= 4\ \{\cos n a_1 + \cos n(a_p+a_q) + \cos n(a_p-a_q) \\ &\quad + \cos n(2a_p+a_1) + \cos n(2a_p-a_1)\} \end{aligned}$$

It is now practicable to see for what combination of values of a_1, a_p and a_q, the ratios of the four structure factors come

out right. By trial it is found that good agreement is obtained when they have the following values :—

$$a_\phi = 2a_1 = 11°$$
$$a_\beta = 56°45'$$

Hence the angle CAE (Fig. 2) is given by

$$\text{Sin CAE} = \frac{CS}{AC} = \frac{CS}{20A} = 1$$
$$\text{or } \angle CAE = 80°$$
$$\text{or } \chi = 0°$$

Thus the longitudinal contraction of the benzene ring, if there be at all any, is not appreciable.

Equating the values of the z-co-ordinates of A and Q thus obtained to their expressions in terms of θ and ϕ, we have

$$5\beta°45' = \frac{1{\cdot}23 \cos(32{\cdot}44'\phi) \times 360°}{7{\cdot}30}$$

$$\text{and, } 5°30' = \frac{0{\cdot}71 \text{ Sin } \theta \text{ (tan } 32{\cdot}44' - \text{Sin} - \phi) \times 360°}{8{\cdot}68}$$

so that,

$$\theta = 25°$$
$$\phi = 12°$$

The only parameter that still remains to be determined is ψ. The reflections that we have considered are independent of ψ and hence other planes are to be considered. Since we have found all the parameters except ψ, we may calculate the intensities for a number of reflections for different values of ψ and see for what value there is agreement with the experimental results. It is seen that the best agreement is obtained when ψ is put equal to zero.

For the determination of the parameters we have so far depended practically on the measurements of the reflections

from the 001 plane and its higher orders, and hence it is necessary to verify how far the above ways of placing the molecule give correct values for the structure factors in other directions as well. The results of varying θ and ϕ are given in Fig. 3. The first two curves show the experimental and the theoretical values of the structure factors, while the other lines are drawn for different values of θ and ϕ.

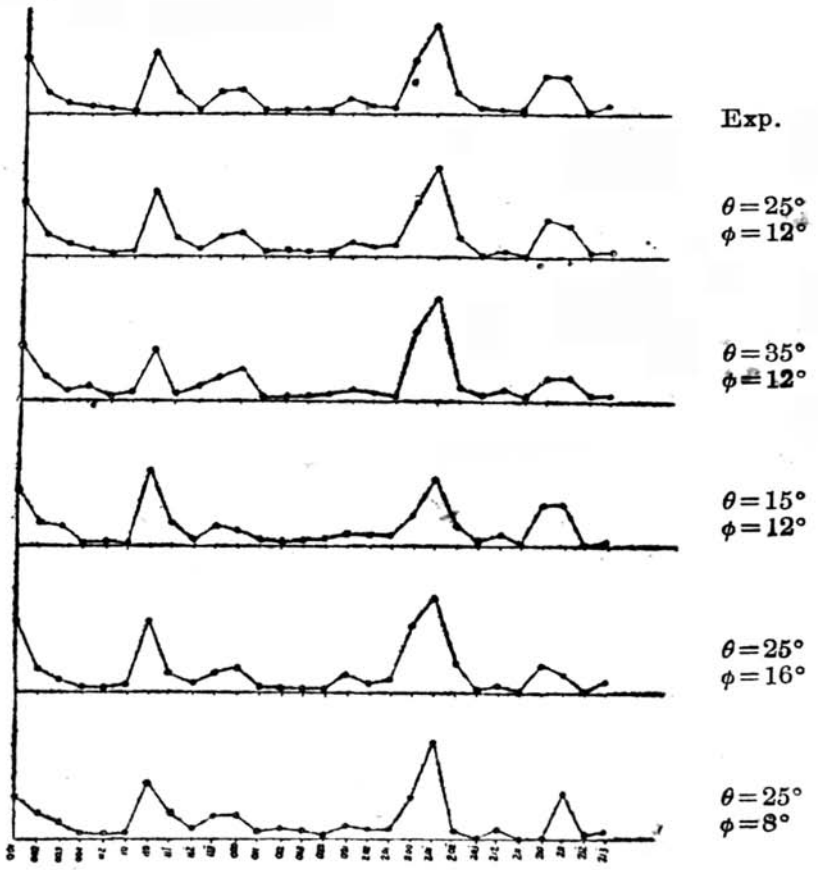

Fig. 3

5. Determinations of the Parameters for Anthracene.

For anthracene the parameters that determine the positions of the atoms are similar to those of naphthalene,

but here one more unknown parameter occurs, namely, the inclination between the different benzene rings in the same molecule. For naphthalene we concluded from symmetry considerations that the two rings must be in the same plane, but here that is not a necessary condition, since, the centre of symmetry may be preserved even if the two side rings are inclined equally at an angle Γ to the middle ring as shown in section in Fig. 5. The symmetry conditions are also not sufficient to decide whether the longitudinal contraction, if there be any, of the side rings are the same as or different from that of the middle ring. The atoms C and G, Fig. 4, however, are similar as regards neighbours and the forces with which they are bound to A may be taken as equal. We may, therefore, consider that the angles BAC and BAG are equal and the sizes of the three rings are the same. Hence the parameters that we are to determine are θ, ϕ, ψ, χ and Γ. These may be found in the same manner as we have done for naphthalene.

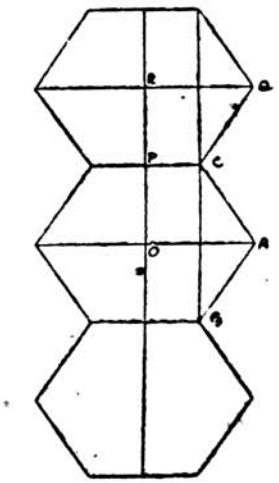

Fig. 4.

The z-co-ordinates of the 28 carbon atoms will have the following pairs of values :—

$$z_1,\ z_2,\ z_3,\ z_4,\ z_5,\ z_6,\ z_7,$$
$$-z_1,\ -z_2,\ -z_3,\ -z_4,\ -z_5,\ -z_6,\ \text{and}\ -z_7.$$

their ratios to c are given by the relations -

$$\rho_1$$
$$\rho_2=\rho_p-\rho_a$$
$$\rho_3=\rho_p-\rho_q$$
$$\rho_4=\rho_q-\rho_p-\rho_1$$
$$\rho_5=\rho_p-\rho_q-\rho_1$$
$$\rho_6=\rho_p-2\rho_q-\rho_a$$
$$\rho_7=\rho_p-2\rho_q-\rho_a$$

where the ratios to the c-axes of the z-co-ordinates of A, P, C, R Fig. 4, are respectively ρ_1, ρ_p, $\rho_p-\rho_a$ and $\rho_p-\rho_q$.

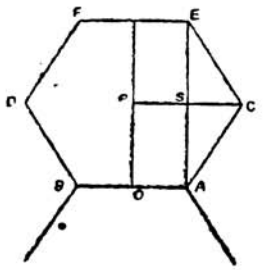

Fig. 5.

The experimental values of the structure factors for the 5 orders of reflections from the $0\bar{0}1$ face are given in Table IV. By trial it was found that the best results were obtained for the combination of values

$$\alpha_1=2\pi\rho_1=10°$$
$$\alpha_p=2\pi\rho_p=44°$$
$$\alpha_q=2\pi\rho_q=44°$$
$$\alpha_a=2\pi\rho_a=0$$

This shows that OP and OR are practically in the same straight line and the benzene rings are regular hexagons. From these values we obtain

$$\theta = 25°$$
$$\phi = 9°$$
$$\chi = 0$$
$$\Gamma = 0$$

In order to determine ψ we compare the intensities of the reflections from the different planes with those calculated for different values of ψ. It is found that the best agreement is obtained here also, when $\psi = 0$. The results are shown in Fig. 6. The first two lines represent the theoretical and the experimental values of the structure factors, while the other two curves are drawn for different values of θ, ϕ being chosen to give the nearest approach to experimental results.

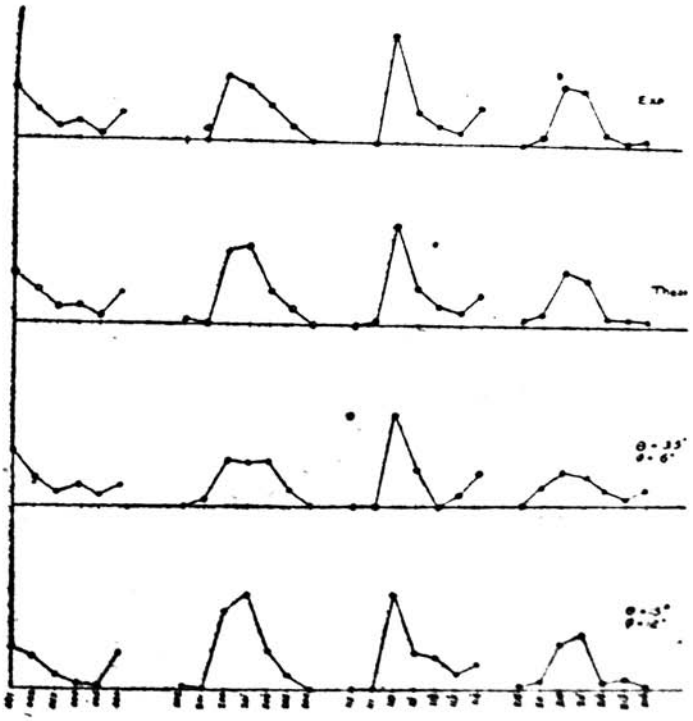

Fig. 6.

6. *Conclusion.*

The accuracy of the above determinations of the orientations of the molecules of naphthalene and anthracene cannot be very great as the intensity measurements are rather rough. Errors as high as 10 per cent. or even more are not improbable in the determinations of the angles that fix the orientations. But so far it is definite that the molecules in naphthalene and anthracene crystals are inclined to the cell faces and none of the crystallographic axes are in the plane of the molecule. The molecules are nearer to the *bc* plane than to any other cell face. The tilting of the molecule from the *c*-axis is evidently due to the action of the β-hydrogens at the ends of the molecules; the longer molecule of anthracene is thus tilted through a smaller angle than naphthalene.

The optical and the magnetic properties demand that the molecules of naphthalene and anthracene should be nearer to the *bc* plane than the *ac* plane. For, the magnetic susceptibility along the normal to the *bc* plane is maximum and the refractive index for the electric vector along the same direction is minimum, which cannot be the case if either '*a*' or the normal to the plane is nearer than '*b*' to the plane of the ring.

That the structure which has been found by the above analysis is consistent with these two facts will be clearer from the following consideration. From parallelism with graphite, let us suppose that for one molecule, the diamagnetic susceptibility is maximum [1] and optical polarisability minimum [2] normal to the benzene ring. Let OP and OQ, Fig 7, be drawn parallel to the normals on the two molecules of the unit cell.

[1] Owen, Ann. d. Phys., Vol. 37, p. 657, 1912; Honda and Take Sone, Sci. Rep. Tohoku Univ., Vol. 2, p. 25, 1913.

[2] Ramanathan, Proc. Roy. Soc., Vol. 110, p. 123, 1920.

Then the plane OP, OQ contains the *b*-axis, the latter bisecting the angle POQ. If ON be the external bisector of the same angle, then in the plane OP, OQ, the maximum diamagnetic susceptibility and minimum optical polarisability will be along ON, while the minimum and maximum respectively of these quantities will be along OB. But ON is very close to the normal to the *bc* plane and hence the structure is in conformity with these results.

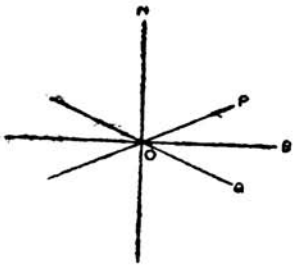

Fig. 7

The author expresses his best thanks to Prof. Sir C. V. Raman, D.Sc., F.R.S., for suggesting the problem and for providing facilities for the work.